(54) Title: BLOCK COPOLYMERS FROM IONIC CATALYSTS

(57) Abstract

A process for the production of block copolymers of ethylene and an α-olefin such as propylene by using an ionic catalyst system including a metallocene component and a component having a cation capable of donating a proton and a compatible non-coordinating anion. Novel block copolymers are produced.

BLOCK COPOLYMERS FROM IONIC CATALYSTS

SPECIFICATION

Cross-Reference to Related Applications

1   This application is a Continuation-in-Part of U.S. Patent
2 Application No. 477,791 filed February 9, 1990. U.S. Patent Application
3 No. 477,791 is in turn a Continuation-in-Part of copending U.S. Patent
4 Application Nos. 133,052 filed December 21, 1987 and 133,480 filed
5 December 22, 1987. Copending U.S. Patent Application No. 133,052 is in
6 turn a Continuation-in-Part of U.S. Patent Application No. 011,471 filed
7 January 30, 1987. Copending U.S. Patent Application No. 133,480 is in
8 turn a Continuation-in-Part of U.S. Patent Application No. 008,800 filed
9 January 30, 1987.

FIELD OF THE INVENTION

10   This invention relates to a method for preparing block and
11 tapered copolymers by polymerizing ethylene and other olefins in the
12 presence of a catalyst which is a reaction product of a metallocene
13 component with second component which comprises a cation capable of
14 donating a proton and a compatible non-coordinating anion. More
15 particularly, this invention relates to a process for the production
16 of mutiblock and tapered copolymers of ethylenically unsaturated
17 monomers. The invention also related to the multiblock and tapered
18 copolymers produced.

BACKGROUND OF THE INVENTION

19   Block copolymers are well known. They have been used
20 commercially as components in adhesives, as melt processable rubbers,

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1 impact resistant thermoplastics, and as compatibilizers, or
2 "surfactants", for emulsifying polymer-polymer blends.
3   There has been widespread interest in polymer blends and
4 alloys. Unfortunately, most homopolymer pairs are immiscible with one
5 another and give rise to low strength materials due to the lack of
6 interfacial adhesion between the separate phases. A block copolymer
7 is created when two or more polymeric segments, or blocks, of
8 different chemical composition are covalently bonded in an end-to-end
9 fashion. Block copolymers have certain advantages over blends.
10 Firstly, the segments are covalently bonded to each other, thereby
11 eliminating the interface problem. Secondly, block copolymers can be
12 used to strengthen blends of immiscible polymers by serving as
13 "emulsifiers," which encourage physical connections between the phase,
14 and thus improve the interfacial adhesion and load transferring
15 capability of the components.
16   While a wide variety of block copolymer architectures are
17 possible, most block copolymers of interest involve the covalent
18 bonding of hard plastic segments which are crystalline or glassy, to
19 elastomeric blocks forming thermoplastic elastomers. Other block
20 copolymers, such as rubber-rubber, glass-glass, and glass-crystalline
21 block copolymers are also possible and may have commercial
22 importance. Two common types of block copolymer structures are the
23 diblock and triblock forms. However, multiblock copolymers, in which
24 more than three segments are bonded together, are also desirable.
25   Triblock and multiblock copolymers have the unique ability of
26 behaving as thermoplastic elastomers, combining thermoplasticity with
27 rubber-like behavior. The key requirements for achieving
28 thermoplastic elastomeric behavior is the ability to develop a
29 two-phase physical network. Such a system is composed of a minor
30 fraction of hard block, having a glass transition temperature (Tg) or
31 melting temperature (Tm) above room temperature, and a major fraction
32 of a soft block, having a Tg below room temperature. The hard blocks
33 associate to form small morphological domains that serve as physical
34 crosslinking and reinforcement sites. These states are thermally
35 reversible making it possible to process the polymer as a melt at

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1 temperatures above the Tg or Tm of the hard block.

2   Block copolymers are similar to, yet distinct from, tapered
3 polymers. In a tapered copolymer the composition of comonomer is
4 gradually varied from one end of the polymer to the other. Tapered
5 copolymers are commercially used as viscosity modifiers, oil
6 additives, thermoplastic elastomers, and impact-resistant plastics.

7   Much work has been done in an attempt to synthesize olefinic
8 block copolymers. The ideal catalyst system would produce a "living
9 polymer." Unlike typical Ziegler-Natta polymerization processes
10 living polymerization processes involve only initiation and
11 propagation steps and are essentially devoid of terminating side
12 reactions. This permits the synthesis of the predetermined and
13 well-controlled structures required for effective block
14 copolymerization. A polymer created in a "living" system can have an
15 extremely narrow distribution of molecular weight and be essentially
16 monodisperse. The living polymer technique is uniquely suited for the
17 preparation of block copolymers. Living catalyst systems are
18 characterized by an initiation rate which is considerably higher than
19 the propagation rate, and the absence of termination or transfer
20 reactions. In addition, these systems are characterized by the
21 presence of a single type of active site.

22   Anionic polymerization routes to ideal olefinic block
23 copolymers have been much studied. Butadiene-isoprene block
24 copolymers have been synthesized using the sequential addition
25 technique. In sequential addition, a certain amount of one of the
26 monomers is contacted with the catalyst. Once the monomer has reacted
27 to extinction, forming the first block, a certain amount of the second
28 monomer species is introduced and allowed to react to form the second
29 block. The process may be repeated as desired using the same or other
30 anionically polymerizable monomers.

31   Ethylene and other alpha-olefins such as propylene and butene
32 are not directly block polymerizable by anionic techniques. Another
33 technique is described by Falk and Schlott in Macromolecules, 1971 4,
34 152. The first step in the procedure involves preparing block
35 polymers containing polybutadiene and polyisoprene using anionic

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1   techniques. The low pressure catalytic hydrogentation of the block
2   polymer obtains the saturated block polymer.
3   The anionic routes to ideal olefinic block copolymers provide
4   a clean route to model block copolymers. However, the method is
5   impractical and is not sufficiently versatile for commercial
6   purposes. For example, the anionic route cannot be used to synthesize
7   HDPE or isotactic polypropylene (i-PP) segments.
8   A coordination technique which has been used to synthesize
9   block copolymers involves the use of vanadium catalysts at low
10 temperatures. Doi et. al., in Macromolecules, 1986, 19, 2896, showed
11 that a catalyst prepared from
12 tris(2-methyl1-1,3-butanedionato)vanadium and Al(C$_2$H$_5$)$_2$Cl in
13 toluene has high reactivity in the living coordination polymerization
14 of propene and that a well-defined diblock copolymer of polypropylene
15 and ethylene-propylene rubber can be prepared by adding ethylene
16 monomer during the living polymerization of propene.
17   While the Doi technique has the advantage over the anionic
18 routes of dispensing with the hydrogenation step, it does require very
19 low temperatures. The block copolymerizations carried out by Doi et.
20 al. were performed at -70 and -60 C. Doi also reported, in H.
21 Kaminsky and H. Sinn (Eds.), Transition Metals and Organometallics as
22 Catalysts for Olefin Polymerization, Springer-Verlag 1988, the living
23 copolymerization, at -78 C, of propylene with 1,5-hexadiene. An
24 additional disadvantage of the technique is that it cannot be used to
25 produce i-PP. Furthermore, and no reports of the production of high
26 density polyethylene (HDPE) via this method have appeared in the
27 literature. The catalyst itself is poorly characterized and unstable.
28   Many claims in the prior art have been made for the
29 production of block polymers in the presence of Ziegler-Natta type
30 catalysts. For example, JP63-712 to Mitsubishi Petrochemicals claims
31 a method of producing a propylene block copolymer using a catalyst
32 including a solid titanium component containing magnesium, titanium,
33 halogen and an electron-donor with an organo-aluminum cocatalyst to
34 prepare homopolypropylene in a first stage reaction, following which
35 in a second stage of reaction bis(cyclopentadienyl) titanium

1 dichloride is added and polymerization is continued in the presence of
2 added ethylene. The propylene block copolymers produced are said to
3 have high rigidity and impact strength and good molding properties.
4   U.S. Patent 4,408,019 to Blunt relates to the use of a
5 catalyst-activator system wherein titanium is the sole metal component
6 to produce block copolymers of ethylene and propylene. The block
7 copolymers have the general formula $(AB)_n A$ wherein A is a
8 crystalline polypropylene block, each B is a random ethylene-propylene
9 copolymer block, and n is an integer from 1 to about 12. The
10 catalyst-activator is described as a combination of titanium
11 trichloride as the catalyst and
12 dimethylbis(methylcyclopentadienyl)titanium as an activator. The
13 amount of ethylene in the block polymer is typically 40-65 wt.% with
14 5-15 wt.% present in the ethylene-propylene segments. The
15 thermoplastic block polymers are said to have superior tensile
16 strength and lower compression set than prior art block polymers. In
17 discussing prior art catalysts, Blunt observes that the production of
18 a true block polymer is dependent upon there being no permanent
19 interruption in the growth of any given polymer chain until all of the
20 blocks have been completed. Moreover, Blunt states that the
21 traditional Ziegler-Natta catalysts based on titanium halides in
22 conjunction with alkylaluminum compounds do not provide a sufficiently
23 long chain lifetime to permit the formation of block copolymers of
24 more than two copolymer blocks.
25   While many patents and publications claim the synthesis of
26 block copolymers from ethylene and propylene, there is no evidence
27 that these products were obtained as well defined block polymers. The
28 known kinetic features of heterogeneous Ziegler-Natta catalysts
29 suggest that it is unlikely that block polymers were synthesized in
30 high concentrations. (J. Boor, Ziegler-Natta Catalysts and
31 Polymerizations, Academic Press 1979). According to Boor, the
32 reported propylene and ethylene block copolymers are most likely
33 mixtures of largely isotactic polypropylene, polyethylene, and either
34 random, block, or tapered copolymers which are present in low
35 concentrations, in the range of 0 to 20%.

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1   As reasons for his conclusion, Boor lists a large number of
2   inherent barriers which must be overcome in using known Ziegler-Natta
3   catalysts to synthesize block copolymers. For example, to synthesize
4   ethylene/α-olefins block copolymers the following conditions must be
5   satisfied: 1) all of the Ti centers must become active
6   simultaneously; 2) all the Ti centers must stay alive during the
7   polymerization; 3) all the Ti centers must have equal activities for
8   polymerizing propylene and ethylene; 4) all the Ti centers must be
9   equally accessible to the available olefin molecules; 5) the
10 cross-over propagation rates must be high for Ti-propylene centers to
11 be efficiently converted into Ti-polyethylene centers; 6) the centers
12 must be isotactic-specific for propylene polymerization and polymerize
13 all ethylene molecules to a linear polymer.
14   Several difficulties arise in the use of known catalysts for
15 the block copolymerization of olefins. Among those are the fact that
16 conventional catalysts are typically multi-sited, and a significant
17 fraction of the active sites are unstable. This leads to random chain
18 initiation and termination which, in turn, lowers the theoretical
19 block copolymer yield. What is desired, and what practice of this
20 invention provides, is a catalyst system with well-characterized
21 structure and reactivity which has a single active site. The system
22 should have well-defined and stable polymerization kinetics and be
23 free of aluminum alkyls or other chain transfer agents.

SUMMARY OF THE INVENTION

24   The invention comprises a process for the production of novel
25 block copolymers of ethylene with an α-olefin and the polymers
26 obtained therefrom. The process includes sequentially contacting
27 ethylene with an α-olefin monomer in a suitable solvent at about 0°C
28 in the presence of an ionic catalyst to produce a block copolymer.
29 Thus, for example, when a-PP-HDPE diblock is produced, the process
30 provides a diblock copolymer yield of 40-70%. The molecular weight of
31 the block copolymer may be controlled by varying the
32 catalyst-to-monomer ratio. The ionic catalyst which is a critical
33 component of the inventive polymerization process, comprises the

1   reaction product of a first component which is a bis(cyclopentadienyl)
2   derivative of a metal of Group IV-B of the Periodic Table of the
3   Elements, which metal is capable of forming a cation formally having a
4   coordination number of 3 and a valence of +4; and at least one second
5   component comprising a cation capable of donating a proton and a
6   compatible non-coordinating anion which anion is bulky and labile, and
7   capable of stabilizing the Group IV-B metal cation without interfering
8   with the ability of said Group IV-B metal cation, or its decomposition
9   product, to polymerize α-olefins to form tapered polymers and
10 multiblock polymers such as di- and tri-block homo-, and copolymers of
11 ethylene and propylene with one or more other alpha-olefins.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

12   The invention provides (1) novel non-random di-, tri-, and
13 multi-block copolymers and tapered copolymers of ethylene, 1-olefins,
14 diolefins, cyclic olefins, acetylenes and other unsaturated monomers;
15 and (2) the processes for polymerizing said non-random copolymers.

Ionic Catalyst System - General Description

16   The process of this invention is practiced with that class of
17 ionic catalysts referred to, disclosed, and described in our copending
18 U.S. Patent Application Nos. 133,052 and 133,480. The ionic catalyst
19 is prepared by combining at least two components. The first of these
20 is a bis(cyclopentadienyl) derivative of a Group IV-B metal compound
21 containing at least one ligand which will combine with the second
22 component or at least a portion thereof such as a cation portion
23 thereof. The second component is an ion-exchange compound comprising
24 a cation which will irreversibly react with at least one ligand
25 contained in said Group IV-B metal compound and a noncoordinating
26 anion which is bulky, labile, and stable. Upon combination of the
27 first and second components, the cation of the second component reacts
28 with one of the ligands of the first component, thereby generating an
29 ion pair consisting of a Group IV-B metal cation with a formal
30 c ordination number of 3 and a valence of +4 and the aforementioned
31 anion, which anion is compatible with and non-coordinating towards the

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1 metal cation formed from the first component. The anion of the
2 second compound must be capable of stabilizing the Group IV-B
3 metal cation complex without interfering with the Group IV-B metal
4 cation's or its composition product's ability to function as a
5 catalyst and must be sufficiently labile to permit displacement by
6 an olefin, diolefin or an acetylenically unsaturated monomer
7 during polymerization.

A.   The Metallocene Component

8 The Group IV-B metal compounds; i.e., titanium, zirconium
9 and hafnium metallocene compounds, useful as first compounds in
10 the preparation of the improved catalyst of this invention are
11 bis(cyclopentadienyl) derivatives of titanium, zirconium and
12 hafnium. In general, useful titanocene, zirconocenes and
13 hafnocenes may be represented by the following general formulae:
14   1. $(A\text{-}Cp)MX_1X_2$
15   2. $(A\text{-}Cp)MX'_1X'_2$
16   3. $(A\text{-}Cp)ML$
17   4. $(Cp^*)(CpR) MX_1$
18 wherein "Cp" represents a cyclopentadienyl radical which may be
19 substituted or unsubstituted, and"
20   (A-cp) is either $(Cp)(Cp^*)$ or $Cp\text{-}A'\text{-}Cp^*$ and Cp and Cp^* are
21   the same or different cyclopentadienyl ring substituted with
22   from zero to five substituent groups R.
23   The substituent groups R may be, independently, selected
24 from a wide variety of classes of radical groups which form
25 covalent bonds to the carbon atoms of the Cp-rings. These
26 substituents act to modify the catalyst behavior by affecting the
27 symmetry, sterics, and electronics of the transition metal center.

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1   Illustrative but not limiting examples of suitable R substituents
2   include hydrocarbyl radicals containing from 1 to 50 carbon atoms;
3   substituted hydrocarbyl radicals wherein one or more of the
4   hydrogen atoms is replaced by a halogen radical, an amido raidcal
5   (X_1X_2N-), a phosphido radical (X_1X_2P-), an alkoxy radical (X_1O) or
6   any other radical containing Lewis acidic or basic functionality;
7   hydrocarbyl substituted metalloid radicals wherein the metalloid
8   is selected from the Group IV-A of the Periodic Table of elements;
9   halogen radicals, amido radicals (X_1X_2N-), phosphido radicals
10   (X_1X_2P-), alkoxy radicals (X_1O), alkylborido radicals (X_1X_2B-), or
11   any other radical containing Lewis acidic or basic functionality;
12   or Cp and/or Cp* are a cyclopentadienyl ring in which two adjacent
13   R groups are joined forming a C_4 to C_{20} ring to give a saturated
14   or unsaturated polycyclic cyclopentadienyl ligand such as indenyl,
15   tetrahydroindenyl, fluorenyl, or octahydrofluorenyl; A' is a
16   covalent bridging group between the two cyclopentadienyl groups; M
17   is titanium, zirconium or hafnium; L is an olefin, diolefin or
18   aryne ligant; X_1 and X_2 are, independently, selected from the
19   group consisting of hydride radicals, hydrocarbyl radicals having
20   from 1 to about 20 carbon atoms, hydrocarbyl radicals wherein one
21   or more of the hydrogen atoms are replaced with a halogen atom,
22   organometalloid radicals comprising a Group IV-A element wherein
23   each of the hydrocarbyl substitutions contained in the organic
24   portion of said organometalloid independently contain from 1 to
25   about 20 carbon atoms and the like; X'_1 and X'_2 are joined and
26   bound to the metal atom to form a metallacycle, in which the metal
27   atom, X'_1 and X'_2 form a hydrocarbocyclic ring containing from
28   about 3 to about 20 carbon atoms; and R is a substituent,
29   preferably a hydrocarbyl substituent, on one of the
30   cyclopentadienyl radicals which is also bound to the metal atom.

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1   Illustrative, but not limiting examples of
2   bis(cyclopentadienyl)zirconium compounds which may be used in the
3   preparation of the improved catalyst of this invention are
4   dihydrocarbyl-substituted bis(cyclopentadienyl)zirconium compounds
5   such as bis(cyclopentadienyl)zirconium dimethyl,
6   bis(cyclopentadienyl)zirconium diethyl, bis(cyclopentadienyl)zirconium
7   dipropyl, bis(cyclopentadienyl)zirconium dibutyl,
8   bis(cyclopentadienyl)zirconium diphenyl,
9   bis(cyclopentadienyl)zirconium dineopentyl,
10   bis(cyclopentadienyl)zirconium di(m-tolyl),
11   bis(cyclopentadienyl)zirconium di(p-tolyl) and the like;
12   (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds such
13   as (methylcyclopentadienyl)(cyclopentadienyl) and
14   bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclopentadienyl)
15   (cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium dimethyl,
16   (propylcyclopentadienyl)(cyclopentadienyl) and
17   bis(propylcyclopentadienyl)zirconium dimethyl,
18   (n-butylcyclopentadienyl) (cyclopentadienyl) and
19   bis(n-butylcyclopentadienyl)zirconium dimethyl,
20   (t-butylcyclopentadienyl) (cyclopentadienyl) and
21   bis(t-butylcyclopentadienyl)zirconium dimethyl,
22   (cyclohexylmethylcyclopentadienyl) (cyclopentadienyl) and
23   bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl,
24   (benzylcyclopentadienyl) (cyclopentadienyl) and
25   bis(benzylcyclopentadienyl)zirconium dimethyl,
26   (diphenylmethylcyclopentadienyl) (cyclopentadienyl) and
27   bis(diphenylmethylcyclopentadienyl)zirconium dimethyl,
28   (methylcyclopentadienyl) (cyclopentadienyl) and
29   bis(methylcyclopentadienyl)zirconium dihydride,
30   (ethylcyclopentadienyl)(cyclopentadienyl) and
31   bis(ethylcyclopentadienyl)zirconium dihydride,
32   (propylcyclopentadienyl)(cyclopentadienyl) and
33   bis(propylcyclopentadienyl)zirconium dihydride,
34   (n-butylcyclopentadienyl)(cyclopentadienyl) and
35   bis(n-butylcyclopentadienyl)zirconium dihydride,
36   (t-butylcyclopentadienyl)(cyclopentadienyl) and

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1   bis(t-butylcyclopentadienyl)zirconium dihydride,
2   (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and
3   bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
4   (benzylcyclopentadienyl)(cyclopentadienyl) and
5   bis(benzylcyclopentadienyl)zirconium dihydride,
6   (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and
7   bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;
8   (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds
9   such as (dimethylcyclopentadienyl) (cyclopentadienyl) and
10 bis(dimethylcyclopentadienyl) zirconium dimethyl,
11 (trimethylcyclopentadienyl) (cyclopentadienyl) and
12 bis(trimethylcyclopentadienyl) zirconium dimethyl,
13 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
14 bis(tetramethylcyclopentadienyl) zirconium dimethyl,
15 (permethylcyclopentadienyl) (cyclopentadienyl) and
16 bis(permethylcyclopentadienyl) zirconium dimethyl,
17 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and
18 bis(ethyltetramethylcyclopentadienyl) zirconium dimethyl,
19 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,
20 (dimethylcyclopentadienyl) (cyclopentadienyl) and
21 bis(dimethylcyclopentadienyl) zirconium dihydride,
22 (trimethylcyclopentadienyl) (cyclopentadienyl) and
23 bis(trimethylcyclopentadienyl) zirconium dihydride,
24 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
25 bis(tetramethylcyclopentadienyl)zirconium dihydride,
26 (permethylcyclopentadienyl) (cyclopentadienyl) and
27 bis(permethylcyclopentadienyl)zirconium dihydride,
28 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and
29 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
30 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium
31 (propylcyclopentadienyl) (cyclopentadienyl) and
32 bis(propylcyclopentadienyl)zirconium dihydride,
33 (n-butylcyclopentadienyl) (cyclopentadienyl) and
34 bis(n-butylcyclopentadienyl)zirconium dihydride,
35 (t-butylcyclopentadienyl) (cyclopentadienyl) and

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1   bis(t-butylcyclopentadienyl)zirconium dihydride,
2   (cyclohexylmethylcyclopentadienyl) (cyclopentadienyl) and
3   bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
4   (benzylcyclopentadienyl) (cyclopentadienyl) and
5   bis(benzylcyclopentadienyl)zirconium dihydride,
6   (diphenylmethylcyclopentadienyl) (cyclopentadienyl) and
7   bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;
8   (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds
9   such as (dimethylcyclopentadienyl) (cyclopentadienyl) and
10 bis(dimethylcyclopentadienyl) zirconium dimethyl,
11 (trimethylcyclopentadienyl) (cyclopentadienyl) and
12 bis(trimethylcyclopentadienyl) zirconium dimethyl,
13 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
14 bis(tetramethylcyclopentadienyl) zirconium dimethyl,
15 (permethylcyclopentadienyl) (cyclopentadienyl) and
16 bis(permethylcyclopentadienyl) zirconium dimethyl,
17 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and
18 bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl,
19 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,
20 (dimethylcyclopentadienyl)(cyclopentadienyl) and
21 bis(dimethylcyclopentadienyl)zirconium dihydride,
22 (trimethylcyclopentadienyl) (cyclopentadienyl) and
23 bis(trimethylcyclopentadienyl)zirconium dihydride,
24 (tetramethylcyclopentadienyl) (cyclopentadienyl) and
25 bis(tetramethylcyclopentadienyl)zirconium dihydride,
26 (permethylcyclopentadienyl)(cyclopentadienyl) and
27 bis(permethylcyclopentadienyl)zirconium dihydride,
28 (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and
29 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
30 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride and
31 the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium
32 compounds such as (trimethylsilylcyclopentadienyl)(cyclopentadienyl)
33 and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,
34 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
35 bis(trimethylgermylcyclopentadienyl)zirconium dimethyl,

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1   (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
2   bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,
3   (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
4   bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,
5   (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and
6   bis(trimethylsilylcyclopentadienyl)zirconium dihydride,
7   (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
8   bis(trimethylgermylcyclopentadienyl)zirconium dihydride,
9   (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
10 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,
11 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
12 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the like;
13 (halogen-substituted-cyclopentadienyl) zirconium compounds such as
14 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
15 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl
16 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
17 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the like;
18 silyl-substituted bis(cyclopentadienyl) zirconium compounds such as
19 bis(cyclopentadienyl) (trimethylsilyl)(methyl)zirconium,
20 bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium,
21 bis(cyclopentadienyl) [tris(dimethylsilyl)silyl](methyl)zirconium,
22 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,
23 bis(cyclopentadienyl)(trimethylsilyl)trimethylsilylmethyl) zirconium,
24 bis(cyclopentadienyl) (trimethylsilylbenzyl) and the like;
25 (bridged-cyclopentadienyl)zirconium compounds such as methylene
26 bis(cyclopentadienyl)zirconium dimethyl,
27 methylene(cyclopentadienyl)zirconium dimethyl, ethylene
28 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl
29 bis(cyclopentadienyl)zirconium dihydride, ethylene
30 bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl
31 bis(cyclopentadienyl)zirconium dihydride and the like; chiral and
32 C$_2$-symmetion compounds; "zirconacycles": assymetrically
33 bridged-dicylopentadienyl compounds such as
34 methylene(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,
35 dimethysily(cyclopentadienyl)(1-fluorenyl)zirconium dihydride,

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1   diphenylmethylene(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,

2   isopropyl(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl,

3   isopropyl(cyclopentadienyl)(1-octahydrofluorenyl)zirconium dihydride,

4   dimethylsilyl(methylcyclopentadienyl(1-fluorenyl)zirconium dihydride,

5   methylene(cyclopentadienyl(tetramethylcyclopentadienyl)zirconium

6   dimethyl and the like: racemic and meso isomers of symmetrically

7   bridged substituted dicyclopentadienyl compounds such as

8   ethylenebis(indenyl)zirconium dimethyl,

9   dimethylsilylbis(indenyl)zirconium dimethyl,

10   ethylenebis(tetrahydroindenyl)zirconium dimethyl,

11   dimethylsilylbis(3-trimethylsilylcyclopentadientyl)zirconium dihydride

12   and the like; zirconacycles such as bis(pentamethylcyclopentadienyl)

13   zirconacyclobutane, bis(pentamethylcyclopentadienyl)

14   zirconacyclopentane, bis(cyclopentadienyl)zirconaindane,

15   1-bis(cyclopentadienyl)zircona-3-dimethylsila-cyclobutane and the

16   like; olefin, diolefin and aryne ligand substituted

17   bis(cyclopentadienyl)zirconium compounds such as bis(cyclopentadienyl)

18   (1,3-butadiene)zirconium, bis(cyclopentadienyl)

19   (2,3-dimethyl-1,3-butadiene)zirconium,

20   bis(pentamethylcyclopentadienyl)(benzyne)zirconium and the like;

21   (hydrocarbyl)(hydride) bis(cyclopentadienyl)zirconium compounds such

22   as bis(pentamethylcyclopentadienyl)zirconium (phenyl)(hydride),

23   bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the

24   like; and bis(cyclopentadienyl) zirconium compounds in which a

25   substituent on the cyclopentadienyl radical is bound to the metal such

26   as (pentamethylcyclopentadienyl)

27   (tetramethylcyclopentadienylmethylene) zirconium hydride,

28   (pentamethylcyclopentadienyl)

29   (tetramethylcyclopentadienylmethylene)zirconium phenyl and the like.

30   A similar list of illustrative bis(cyclopentadienyl) hafnium

31   and bis(cyclopentadienyl)titanium compounds could be made, but since

32   the lists would be nearly identical to that already presented with

33   respect to bis(cyclopentadienyl)zirconium compounds, such lists are

34   not deemed essential to a complete disclosure. Other

35   bis(cyclopentadienyl)hafnium compounds and other

36   bis(cyclopentadienyl)titanium compounds as well as other

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1 bis(cyclopentadienyl)zirconium compounds which are useful in the
2 catalyst compositions of this invention will, of course, be apparent
3 to those skilled in the art.
4
5 B.   The Activator Component

6   Compounds useful as an activator component in the preparation
7 of the catalyst of this invention will comprise a cation, which is a
8 Bronsted acid capable of donating a proton, and a compatible
9 noncoordinating anion which anion is relatively large (bulky), capable
10 of stabilizing the active catalyst species (the Group IV-B cation)
11 which is formed when the two compounds are combined and said anion
12 will be sufficiently labile to be displaced by olefinic, diolefinic
13 and acetylenically unsaturated substrates or other neutral Lewis bases
14 such as ethers, nitriles and the like. In general, suitable anions for
15 the second component may be any stable and bulky anionic complex having
16 the following molecular attributes: 1) the anion should have a
17 molecular diameter greater than 4A; 2) the anion should form stable
18 ammonium salts; 3) the negative charge on the anion should be
19 delocalized over the framework of the anion or be localized within the
20 core of the anion; 4) the anion should be a relatively poor
21 nucleophile; and 5) the anion should not be a powerful reducing or
22 oxidizing agent. Anions meeting these criteria - such as polynuclear
23 boranes, carboranes, metallacarboranes, polyoxoanions and anionic
24 coordination complexes are well described in the chemical literature.
25 Two classes of compatible non-coordinating anions meeting these criteria
26 have been disclosed in our copending US Patent Applications Nos. 133,052
27 and 133,480: 1) anionic coordination complexes comprising a plurality
28 of lipophilic radicals covalently coordinated to and shielding a central
29 charge-bearing metal or metalloid core, and 2) anions comprising a
30 plurality of boron atoms such as carboranes, metallacarboranes and
31 boranes.
32   In general, the activator compounds containing single anionic
33 coordination complexes which are useful in this invention may be
34 represented by the following general formula:

35   5. $[(L'-H)^+]_d[(M')^{m+}Q_1Q_2\ldots Q_n]^{d-}$
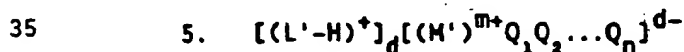
1   Wherein:

2   L' is a neutral Lewis base;

3   H is a hydrogen atom;

4   [L'-H] is a Bronsted acid;

5   M' is a metal or metalloid selected from the Groups
6 subtended by Groups V-B to V-A of the Periodic Table of the Elements;
7 i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;
8   Q_1 to Q_n are selected, independently, from the
9 time, hydrocarbyl radicals containing from 1 to about 20 carbon atoms,
10 substituted-hydrocarbyl radicals, wherein one or more of the hydrogen
11 atoms is replaced by a halogen atom, containing from 1 to about 20
12 carbon atoms, hydrocarbyl-substituted metal (organometalloid) radicals
13 wherein each hydrocarbyl substitution contains from 1 to about 20
14 carbon atoms and said metal is selected from Group IV-A of the
15 Periodic Table of the Elements and the like.

16   In general, Ar_1 and Ar_2 may, independently, be any
17 aromatic or substituted-aromatic hydrocarbon radical containing from
18 about 6 to about 20 carbon atoms. Suitable aromatic radicals include,
19 but are not limited to, phenyl, naphthyl and anthracenyl radicals.
20 Suitable substituents on the substituted-aromatic hydrocarbon
21 radicals, include, but are not necessarily limited to, hydrocarbyl
22 radicals, organometalloid radicals, alkoxy radicals, alkylamido
23 radicals, fluoro and fluorohydrocarbyl radicals and the like such as
24 those useful as X_3 and X_4. The substituent may be ortho, meta
25 or para, relative to the carbon atoms bonded to the boron atom. When
26 either or both X_3 and X_4 are a hydrocarbyl radical, each may
27 be the same or a different aromatic or substituted-aromatic radical as
28 are Ar_1 and Ar_2, or the same may be a straight or branched
29 alkyl, alkenyl or alkynyl radical having from 1 to about 20 carbon
30 atoms, a cyclic hydrocarbon radical having from about 5 to about 8
31 carbon atoms or an alkyl-substituted cyclic hydrocarbon radical having
32 from about 6 to about 20 carbon atoms. X_3 and X_4 may also,
33 independently, be alkoxy or dialkylamido radicals wherein the alkyl
34 portion of said alkoxy and dialkylamido radicals contain from 1 t
35 about 20 carbon atoms, hydrocarbyl radicals and organometalloid
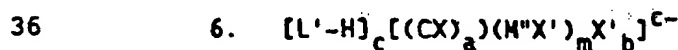36 radicals having from 1 to about 20 carbon atoms and the like. As

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1 indicated above, Ar$_1$ and Ar$_2$ may be linked to each other.
2 Similarly, either or both of Ar$_1$ and Ar$_2$ could be linked to
3 either X$_3$ or X$_4$. Finally, X$_3$ or X$_4$ may also be linked
4 to each other through a suitable bridging group.
5   Illustrative, but not limiting, examples of boron compounds
6 which may be used as an activator component in the preparation of the
7 improved catalysts of this invention are trialkyl-substituted ammonium
8 salts such as triethylammonium tetra(phenyl)boron, tripropylammonium
9 tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron,
10 trimethylammonium tetra(p-tolyl)boron, trimethylammonium
11 tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron,
12 tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium
13 tetra(m,m-dimethylphenyl)boron, tributylammonium
14 tetra(p-tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium
15 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as
16 N,N-dimethylanilinium tetra(pentafluoro phenyl)boron,
17 N,N-diethylanilinium tetra(phenyl)boron,
18 N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like;
19 dialkyl ammonium salts such as di(i-propyl)ammonium
20 tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron
21 and the like; and triaryl phosphonium salts such as
22 triphenylphosphonium tetra(phenyl)boron, tri(methylphenyl)phosphonium
23 tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron
24 and the like.
25   Similar lists of suitable compounds containing other metals
26 and metalloids which are useful as activator components may be made,
27 but such lists are not deemed necessary to a complete disclosure. In
28 this regard, it should be noted that the foregoing list is not
29 intended to be exhaustive and that other useful boron compounds as
30 well as useful compounds containing other metals or metalloids would
31 be readily apparent to those skilled in the art from the foregoing
32 general equations.
33   Activator components based on anions which contain a
34 plurality of boron atoms may be represented by the following general
35 formulae:

36   6. $[L'-H]_c[(CX)_a(H''X')_m X'_b]^{c-}$

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1   7. $[L'-H]_d[[[(CX_3)_a \cdot (M''X_4)_m \cdot (X_5)_b]^{c-}]_2 M^{n+}]^{d-}$
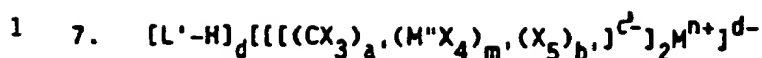
2   wherein $[L'-H]$ is either H^+, ammonium or a substituted
3   ammonium cation having up to 3 hydrogen atoms replaced with a
4   hydrocarbyl radical containing from 1 to about 20 carbon atoms or a
5   substituted-hydrocarbyl radical, wherein one or more of the hydrogen
6   atoms is replaced by a halogen atom, containing from 1 to about 20
7   carbon atoms, phosphonium radicals, substituted-phosphonium
8   radicals having up to 3 hydrogen atoms replaced with a hydrocarbyl
9   radical containing from 1 to about 20 carbon atoms or a
10   substituted-hydrocarbyl radical, wherein 1 or more of the hydrogen
11   atoms is replaced by a halogen atom, containing from 1 to about 20
12   carbon atoms and the like; C is carbon; M'' is boron or phosphorus;
13   each of X, X', X'', X_3, X_4 and X_8 are radicals selected,
14   independently, from the group consisting of hydride radicals, halide
15   radicals, hydrocarbyl radicals containing from 1 to about 20 carbon
16   atoms, substituted-hydrocarbyl radicals, wherein one or more of the
17   hydrogen atoms is replaced by a halogen atom, containing from 1 to 20
18   carbon atoms, organometalloid radicals wherein each hydrocarbyl
19   substitution in the organo portion contains from 1 to about 20 carbon
20   atoms and said metal is selected from Group IV-A of the Periodic
21   Table of the Elements and the like; M is a transition metal; "a" and
22   "b" are integers ≥ 0; "c" is an integer ≥ 1; a + b + c = an
23   even-numbered integer from 2 to about 8; and "m" is an integer
24   ranging from 5 to about 22; "a'" and "b'" are the same or a different
25   integer ≥ 0; "c'" is an integer ≥ 2; a' + b' + c' = an
26   even-numbered integer from 4 to about 8; "m'" is an integer from 6 to
27   about 12; "n" is an integer such that 2c' - n = d; and "d" is an
28   integer greater than or equal to 1.
29   Illustrative, but not limiting, examples of second
30   components which can be used in preparing catalyst systems utilized
31   in the process of this invention wherein the anion of the second
32   component contains a plurality of metalloid atoms (as in formulae 5
33   and 6) are ammonium salts such as ammonium 1-carbadodecaborate (using
34   1-carbadodecaborate as an illustrative, but not limiting, counterion
35   for the ammonium cations listed below): monohydrocarbyl-substituted
36   ammonium salts such as methylammonium 1-carbadodecaborate,
37   ethylammonium 1-carbadodecaborate, propylammonium

1 1-carbadodecaborate, isopropylammonium 1-carbadodecaborate,
2 (n-butyl)ammonium 1-carbadodecaborate, anilinium 1-carbadodecaborate,
3 and (p-tolyl)ammonium 1-carbadodecaborate and the like;
4 dihydrocarbyl-substituted ammonium salts such as dimethylammonium
5 1-carbadodecaborate, diethylammonium 1-carbadodecaborate,
6 dipropylammonium 1-carbadodecaborate, diisopropylammonium
7 1-carbadodecaborate, di(n-butyl) ammonium 1-carbadodecaborate,
8 diphenylammonium 1-carbadodecaborate, di(p-tolyl)ammonium
9 1-carbadodecaborate and the like; trihydrocarbyl-substituted ammonium
10 salts such as trimethylammonium 1-carbadodecaborate, triethylammonium
11 1-carbadodecaborate, tripropyl-ammonium 1-carbadodecaborate,
12 tri(n-butyl) ammonium 1-carbadodecaborate, triphenylammonium
13 1-carbadodecaborate, tri(p-tolyl)ammonium 1-carbadodecaborate,
14 N,N-dimethylanilinium 1-carbadodecaborate, N,N-diethylanilinium
15 1-carbadodecaborate and the like.
16   Illustrative, but not limiting examples of second compounds
17 corresponding to Formula 5 [using tri(n-butyl)ammonium as an
18 illustrative, but not limiting, counterion for the anions listed
19 below] are salts of anions such as bis[tri(n-butyl)ammonium]
20 nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)
21 ammonium]undecaborate, bis[tri(n-butyl)ammonium] dodecaborate,
22 bis[tri(n-butyl)ammonium]decachlorodecaborate, tri(n-butyl)ammonium
23 dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate,
24 tri(n-butyl) ammonium 1-carbaundecaborate, tri(n-butyl)ammonium
25 1-carbadodecaborate, tri(n-butyl)ammonium
26 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium
27 dibromo-1-carbadodecaborate and the like; borane and carborane
28 complexes and salts of borane and carborane anions such as
29 decaborane(14), 7,8-dicarbaundecaborane(13),
30 2,7-dicarbaundecaborane(13),
31 undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane,
32 dodecahydrido-11-methyl-2,7-di-carbaundecaborane, tri(n-butyl)
33 ammonium undecaborate(14), tri(n-butyl)ammonium
34 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate(13),
35 tri(n-butyl)ammonium 7,8-dicarbaundecaborate(12),

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1 tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),
2 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaundecaborate,
3 tri(n-butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,
4 tri(n-butyl) ammonium undecahydrido-8-butyl-7,9-dicarbaundecaborate,
5 tri(n-butyl)ammonium undecahydrido-8-allyl-7,9-dicarbaundecaborate,
6 tri(n-butyl)ammonium
7 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,
8 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate
9 and the like; boranes and carboranes and salts of boranes and
10 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanonaborane(13),
11 6,9-dicarbadecaborane(14),
12 dodecahydrido-1-phenyl-1,3-dicarbanonaborane,
13 dodecahydrido-1-methyl-1,3-dicarbanonaborane,
14 undecahydrido-1,3-dimethyl-1,3-dicarbanonaborane and the like.
15   Illustrative, but not limiting, examples of second compounds
16 corresponding to Formula 7 [using tri(n-butyl)ammonium as an
17 illustrative, but not limiting, counterion for the anions listed
18 below] are salts of metallacarborane and metallaborane anions such as
19 tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)
20 cobaltate(III), tri(n-butyl)ammonium
21 bis(undeca-hydrido-7,8-dicarbaundecaboratoferrate(III), tri(n-butyl)
22 ammonium bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III),
23 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato)
24 nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,
25 8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium
26 bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)chromate(III),
27 tri(n-butyl)ammonium
28 bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III),
29 tri(n-butyl)ammonium bis(dodecahydridodicarbadodecaborato)
30 cobaltate(III), tris[tri(n-butyl)ammonium] bis
31 (undecahydrido-7-carbaundecaborato)chromate(III),

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1   bis[tri(n-butyl) ammonium]
2   bis(undecahydrido-7-carbaundecaborato)manganate(IV),
3   bis[tri(N-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)
4   cobaltate(III), bis[tri (n-butyl)ammonium] .
5   bis(undecahydrido-7-carbaundecaborato) nickelate(IV) and the like. A
6   similar list of representative phosphonium compounds can be recited
7   as illustrative second compounds, but for the sake of brevity, it is
8   simply noted that the phosphonium and substituted-phosphonium salts
9   corresponding to the listed ammonium and substituted-ammonium salts
10 could be used as second compounds in the present invention.

Choice of Metallocene-Activator Pairs

11   In general, and while most metallocene components identified
12 above may be combined with most activator components identified above
13 to produce an active olefin polymerization catalyst, it is important
14 for continuity of the polymerization operations that either the metal
15 cation initially formed from the metallocene component or a
16 decomposition product thereof be a relatively stable catalyst. It is
17 also important that the anion of the activator compound be stable to
18 hydrolysis when an ammonium salt is used. Further, it is important
19 that the acidity of the activator component be sufficient, relative
20 to the metallocene component, to facilitate the needed proton
21 transfer. Activator compounds containing aryl-ammonium salts such as
22 N,N-dimethylanilium are more acidic than trialkylammonium salts and
23 therefore are useful with a wider variety of metallocene components.
24 The basicity of the metal complex must also be sufficient to
25 facilitate the needed proton transfer. In general,
26 bis(cyclopentadienyl)metal compounds which can be hydrolyzed by
27 aqueous solutions can be considered suitable as metallocene
28 components to form the catalysts described herein.
29   The chemical reactions which occur may be represented by
30 reference to the general formulae set forth herein as follows:

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1 A. $(A-Cp)MX_1X_2 + [L'-H]^+[B']^- \rightarrow [(A-Cp)MX_1]^+[B']^- + HX_2 + L'$ or
2 $\qquad\qquad [(A-Cp)MX_2]^+[B']^- + HX_1 + L'$

3 B. $(A-Cp)M\overline{X'_1X'}_2 + [L'-H]^+[B']^- \rightarrow [(A-Cp)MX'_1X'_2H]^+[B']^- + L'$ or
4 $\qquad\qquad [(A-Cp)MX'_2X'_1H]^+[B']^- + L'$

5 C. $(A-Cp)ML + [L'-H]^+[B']^- \rightarrow [(A-Cp)M(LH)]^+[B']^- + L'$

6 D. $(Cp^*)(\overline{RCp})MX_1 + [L'-H]^+[B']^- \rightarrow [(Cp^*)(HR-Cp)MX_1]^+[B']^- + L'$ or
$\qquad\qquad [(Cp^*)(\overline{R-Cp})M]^+[B']^- + HX_1 + L'$

7   In the foregoing reaction equations, the letters A-D
8 correspond to the numbers 1-4, respectively, set forth in combination
9 with the general equations for useful metallocene compounds. B'
10 represents a compatible ion corresponding to the general formulae
11 outlined in formulae 5, 6 and 7 above. When the metallocene and
12 activator components used to prepare the improved catalysts of the
13 present invention are combined in a suitable solvent or diluent, all
14 or a part of the cation of the activator (the acidic proton) combines
15 with one of the substituents on the metallocene compound. In the case
16 where the metallocene component has a formula corresponding to that of
17 general formula 1, a neutral compound is liberated, which neutral
18 compound either remains in solution or is liberated as a gas. In this
19 regard, it should be noted that if either X_1 or X_2 in the
20 metallocene component is a hydride, hydrogen gas may be liberated.
21 Similarly, if either X_1 or X_2 is a methyl radical, methane may
22 be liberated as a gas. In the cases where the first component has a
23 formula corresponding to those of general formulae 2, 3 or 4
24 (optional), one of the substituents on the metallocene component is
25 protonated but no substituent is liberated. In general, the stability
26 and rate of formation of the products in the foregoing reaction
27 equations will vary depending upon the choice of the solvent, the
28 acidity of the $[L'-H]^+$ selected, the particular L', the anion, the
29 temperature at which the reaction is completed and the particular
30 cyclopentadienyl derivative of the metal selected.
31   With respect to the combination of the metallocene component
32 with the activator component to form a catalyst of this invention, it

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1 should be noted that the two compounds combined for preparation of the
2 active catalyst must be selected so as to avoid transfer of a fragment
3 of the anion to the metal cation, thereby forming a catalytically
4 inactive species. This could be done by steric hindrance, resulting
5 from substitutions on the cyclopentadienyl carbon atoms as well as
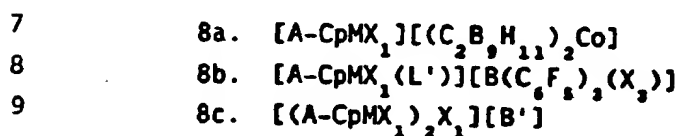6 substitutions on the non-coordinating anion.
7   It follows, then, that the metallocene components comprising
8 perhydrocarbyl-substituted cyclopentadienyl radicals could be
9 effectively used with a broader range of activator compounds than
10 could metallocene components comprising unsubstituted cyclopentadienyl
11 radicals.
12   As the amount and size of the substitutions on the
13 cyclopentadienyl radicals are reduced, however, more effective
14 catalysts are obtained with activator compounds containing
15 non-coordinating anions which are larger in size and more resistant to
16 degradation. In the case where the non-coordinating anion is an
17 anionic coordination complex, such as a tetraphenylboron derivative,
18 substitutions on the phenyl rings can be used to prevent the transfer
19 of a proton or an entire phenyl group from the anion to the metal.
20 This can be accomplished by alkyl substitution in the ortho positions
21 of the phenyl groups, or, more preferably, by perfluoro-substitutions
22 on the anion. Thus, anionic coordination complexes containing
23 perfluorphenyl-, trifluoromethylphenyl-, or bis-trifluormethylphenyl
24 rings are preferred for this subgenus of activator components. When
25 the non-coordinating anion contains a plurality of boron atoms as
26 described in general formulae 6 and 7, more effective catalysts are
27 obtained with activator compounds containing larger anions, such as
28 those encompassed by Equation 7 and those having larger m values in
29 Equation 6. In these cases it is further preferable when using second
30 compounds which are encompassed by Equation 6, that a + b + c = 2.
31 Second compounds in which a + b + c = even-numbered integers of 4 or
32 more have acidic B-H-B moieties which can react further with the metal
33 cation formed, leading to catalytically inactive compounds.
34   As indicated supra, most metallocene compounds will combine
35 with most activator compounds to give an active polymerization

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1 catalyst. The initially formed catalyst is not, however, always
2 sufficiently stable as to permit its separation and subsequent
3 identification. However, catalysts which are thermally stable are
4 preferred for the production of block or tapered copolymers. Three
5 structurally distinct forms of thermally stable ionic catalysts have
6 been identified by NMR spectroscopy and are shown below in equation 8.

7   8a. $[A\text{-}CpMX_1][(C_2B_9H_{11})_2Co]$
8   8b. $[A\text{-}CpMX_1(L')][B(C_6F_5)_3(X_3)]$
9   8c. $[(A\text{-}CpMX_1)_2X_1][B']$

10 In the foregoing reactions the symbols A-Cp, M, X_1, L' and X_3
11 correspond to the definitions set forth in equations 1-4 and 5-5a,
12 respectively; B' represents a compatible non-coordinating anion
13 corresponding to the general formulae set forth in equations 5, 6 and
14 7. In example 8a, NMR spectroscopy indicates that the
15 metallacarborane anion is weakly bound to the metal center; the
16 biproduct L' does not form an observable coordination complex with the
17 metallocene center. In 8b, NMR experiments indicate that the
18 fluorinated boron anion is completely non-coordinating and that L',
19 weakly coordinates to and stabilizes the metallocene cation when the
20 tertiary amine (L') is an aniline derivative. The ability of L' to
21 coordinate to the metal is important to the stability of the catalyst
22 systems which have highly noncoordinating anions. The Lewis basicity
23 of the L' can affect the rate of polymerization and other
24 polymerization parameters. Experience has shown that when the bulk of
25 the amine or the metallocene cation is increased by substitutions on
26 the nitrogen atom or the cyclopentadienyl ligands respectively, the
27 ability for the amine to coordinate to the metal center decreases.
28 Addition of excess metallocene $ACpM(X_1)_2$ to 8a or 8b results
29 in displacement of the anion in 8a or the aniline ligand in 8b to form
30 a stable dimeric cation 8c.

1   <u>Preferred Catalysts For the Production of Block and Tapered</u>
2 <u>Copolymers</u>
3   Ideal catalyst systems for the production of block copolymers
4 are single-sited living catalysts. Living catalysts are those systems
5 in which chain transfer is nonexistent and the rate of initiation is
6 fast compared to propagation. Catalysts which have finite chain
7 transfer rates may also be useful for the production of block and
8 tapered copolymers if the rate of propagation is fast relative to
9 termination. It is also important that the average chain lifetimes
10 are reasonably long (minutes to hours) in order to permit adequate
11 time for modifications of the reactor conditions (e.g. changing
12 monomer feed streams). While most reasonably stable ionic catalysts
13 described above will under suitable conditions produce block and/or
14 tapered copolymers of nonpolar olefins, it is preferred that the
15 catalyst be: 1) thermally stable (recoverable as a single
16 organometallic complex), 2) versatile in terms of random copolymer
17 synthesis (i.e. capable of preparing HDPE, i-PP, s-PP, EP-rubber,
18 LLDPE etc.), 3) capable of producing high molecular weight polymers at
19 reasonable temperatures and pressures, 4) high activity (fast
20 propagation catalysts) and 5) slow in chain termination reactions so
21 that few chains of polymer product are produced per hour per site.
22   Ionic catalysts of the form $[A-CpHMe(L')][B(C_6F_5)_3(X_3)]$ are
23 the preferred catalysts for the production of block and tapered
24 copolymers of ethylene, 1-olefins, dienes, cyclic olefins and other
25 unsaturated monomers. Ionic catalysts of this form where M = Hf are
26 the most preferred catalyst systems because they are more stable,
27 produce higher molecular weight copolymers, and have longer chain
28 lifetimes than corresponding Zr or Ti-based systems. Polymerizations
29 using hafnium systems of this form under standard random copolymer
30 conditions as described in our copending U.S. Patent Application No.
31 133,480 produce high molecular weight HDPE, LLDPE, a-PP, i-PP, s-PP,
32 and EP-rubber at rates comparable to similar Zr-based catalysts.
33 Tapered and block copolymers containing these segments can be
34 produced using the appropriate hafnium ionic catalyst using the
35 techniques and process conditions set forth in the following sections.

1   <u>Processes For the Production of Block and Tapered Copolymers</u>
2   Many procedures for modifying the reactor conditions and
3   monomer feeds for the production of block copolymers have been
4   developed and applied using conventional Ziegler-Natta catalysts.
5   The patent literature concerning block copolymer from Ziegler-Natta
6   catalysts disclose a variety of processes for altering reactor
7   conditions. The processes include batch reactors and sequential
8   additions techniques, series batch reactors, loop and tubular
9   reactors, and fluidized bed reactors. A review of the processes and
10 patents is given in chapter 4 of "Block Copolymers" [D. C. Allport
11 and W. H. James; John Wiley and Sons, New York 1973]. As indicated
12 supra, the application of these processes using conventional
13 catalysts in general produces broad molecular weight distributions of
14 poorly defined polymer blends. In principle, the catalysts of this
15 invention can be used in any of the processes described above for the
16 production well-defined block copolymers of higher purity than
17 obtained using conventional Ziegler-Natta catalysts.
18   The most demanding process, that is the process which
19 requires the longest chain lifetimes, is the sequential addition.
20 When the catalyst or initiator produces growing chains with
21 sufficiently long lifetimes, the sequential addition technique allows
22 for the production of block copolymers having non-tapered transitions
23 between different polymer segments. Sequential addition techniques
24 are commonly used to produce styrenic block copolymers (Kraton for
25 example) using anionic initiators.
26   In the first step of the sequential addition process
27 employed in accordance with this invention the catalyst is placed in
28 a well stirred batch reactor in a suitable solvent and first segment
29 of the block copolymer is grown by adding a specific number of molar
30 equivalents of monomer(s). The catalyst consumes all of the
31 monomer(s) prior to addition of the second monomer(s) (a different
32 set of monomers than in the first step). This procedure can be
33 repeated to prepare multiblock copolymers.
        <u>Sequential Addition Conditions</u>
34   For a given catalyst and target block or tapered copolymer a

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1 solvent, temperature and catalyst concentration must be chosen so
2 that 1) narrow molecular weight distribution, high molecular weight
3 copolymer segments can be synthesized; and 2) the molecular weight of
4 the copolymer segments can be controlled by varying the
5 catalyst-to-monomer molar ratio. Under these conditions the system
6 is behaving in a quasiliving fashion (i.e. slow chain transfer) and
7 narrow molecular weight block copolymers can be prepared in high
8 yield. Methods for choosing the conditions for a particular catalyst
9 system are given below.

Solvent

10   Preferably, the solvent should normally disperse or dissolve
11 the catalyst to form a well-mixed system. The most preferred
12 catalysts for block copolymer synthesis,
13 [ACpHfMe(L')][B(C$_6$F$_5$)$_4$], are prepared in toluene and form non-misible,
14 toluene-dispersible phases. This two-component phase contains the
15 catalyst and a particular amount of toluene; the concentration of
16 toluene in the catalyst phase depends on temperature and the structure
17 of the catalyst. Addition of an aliphatic
18 hydrocarbon to the toluene-catalyst emulsion causes immediate
19 precipitation of the catalyst from solution to give a soft waxy,
20 non-dispersible catalyst deposit. While aliphatic hydrocarbons,
21 fluorinated hydrocarbons, and chlorinated aromatic hydrocarbons may
22 be used in this invention, the preferred solvents for the preparation
23 of block copolymers from the most preferred catalysts are aromatic
24 hydrocarbons such as toluene, xylene, ethyl benzene and the like.
25 The lack of solubility or compatibility of the catalyst phase in the
26 aromatic solvent does not present significant problems in terms of
27 molecular weight broadening because the phase is highly dispersible
28 even at lower temperatures.

Temperature

29   The reactor temperature strongly affects the yield of block
30 copolymer and must be adjusted depending on the type and
31 concentration of monomers and catalyst used. The general procedure
32 for determining this condition is to 1) find the maximum temperature
33 where high molecular weight polymer segments can be prepared and 2)

1 confirm the molecular weight is controlled by the catalyst-to-monomer
2 ratio at this temperature. The general trend is that higher
3 temperatures cause chain transfer to be more rapid relative to
4 propagation and therefore give lower block copolymer yields. The
5 process may be carried out at temperatures of -80°C to 80°C, however,
6 it is preferred that the temperature be in the range of -10°C to
7 20°C.

Concentration of Catalyst

8   The concentration should be high enough to produce
9 significant rates of polymerization under the generally low pressure
10 conditions of sequential addition. The concentration should not be
11 so high as to produce uncontrollable exotherms upon exposure to the
12 monomer. The exotherm can be controlled, however, by adjusting the
13 rate of monomer addition during the formation of a block segment.
14 This level of control allows for a large range of acceptable
15 catalysts concentrations. The process may be carried out at catalyst
16 concentrations ranging from about 6×10^{-6} to about 6×10^{-2}
17 moles of catalyst/liter of solution, however it is preferred that
18 catalyst levels be in the range of 1×10^{-4} to about 3×10^{-3}
19 moles of catalyst/liter of solution.

Monomer Concentration

20   The amount of monomer added depends on the molecular weight
21 of the targeted polymer and the moles of active catalyst in the
22 reactor. Molar ratios of monomer to catalyst may be in the range of
23 about 10:1 to about 10,000:1. The monomers may be added quickly or
24 may be metered in to the reactor to control exotherms.

Order of Monomer Addition

25   Precipitation of polymer (with catalyst attached) causes
26 undesirable broadening of the molecular weight distribution due to
27 mass transport limitations and poor mixing. It is therefore
28 preferred to prepare the soluble block (generally the elastomeric
29 segment) in the first stage of the reaction. Thus, as indicated in
30 the examples, when ethylene is added in the first step in the
31 synthesis of a HDPE-b-atactic-PP diblock copolymer the initially
32 formed polyethylene precipitates with the catalyst and the final

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1 molecular weight distribution of crude block copolymer product is
2 rather broad (Mw/Mn = 3.0). Addition of propylene in the first step
3 produces a system which remains homogeneous throughout the block
4 copolymer synthesis, yielding a crude product having a much narrower
5 MwMn = (1.7 - 1.8).

Preparation of Tapered and Random Copolyers

6   Addition of stoichiometric amounts of a mixture of two
7 olefins to the reactor under block copolymer conditions will
8 naturally produce tapered copolymer because the monomers will
9 generally have different reactivities with the catalyst. Thus, the
10 head of the polymer will be rich in the more reactive comonomer while
11 the polymer tail will contain larger amounts of the slower reacting
12 comonomer. The extent of tapering will depend on magnitude of the
13 difference of monomer reactivity. The extent of tapering can be
14 controlled by metering the two monomers into the reactor at different
15 rates.

16   Random copolymers such as non-crystalline ethylene-propylene
17 rubber can be made under block copolymer conditions by adding the
18 fast monomer (ethylene) to the catalyst/propylene mixture at a rate
19 where the desired amount of ethylene has been added when all the
20 propylene has been consumed. This procedure is exemplified for a
21 ethylene-propylene elastomer containing 50 mole % propylene.

Block Copolymer Products

22   The novel polymer products of this invention are olefinic
23 block and tapered copolymers having narrow molecular weight
24 distributions and well defined di-, tri-, multiblock or tapered
25 structures. The polymer segments which can be incorporated into
26 these architectures include 1) elastomers such as atactic
27 polypropylene, atactic poly-1-olefins, and ethylene/1-olefin
28 copolymers wherein the ethylene comonomer is a C_3-C_{18}
29 α-olefin such as ethylene-propylene, ethylene butene, and
30 ethylene-octene copolymers ethylene-propylene-diene terpolymers and
31 other crosslinkable elastomeric olefins; 2) thermoplastics such as
32 high density polyethylene, linear low density polyethylene having
33 melting points from 80-135°C (e.g. ethylene-propylene and other

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1   ethylene-1-olefin copolymers wherein each 1-olefin has from about 4
2   to 20 carbon atoms), ethylene/diene copolymers such as
3   ethylene/ethyldiene-norbornene copolymers, isotactic polypropylene
4   having melting points from 100°C-165°C, syndiotactic polypropylenes
5   having melting points from 100°C-165°C, hemi-isotactic polypropylenes
6   and other crystalline 1-olefin homo and copolymers; and 3) glasses
7   such as homo-polycyclopentene, homopolynorbornene and the like. The
8   average molecular weight of the polymer segments included in the
9   novel block copolymers of this invention can be in the range of from
10 100-1,000,000 daltons, preferably from 30,000 to 200,000 daltons.
11 The molecular weight distributions (Mw/Mn) of the crude and/or
12 fractionated block copolymer are in the range from about 1.0 to about
13 5.0, preferable from about 1.1 to about 2.0. As indicated above and
14 in the examples following the percentage of block copolymer in the
15 crude product can vary from about 1% to 100%, preferably from about
16 50% to about 90% depending on the application and the conditions of
17 the experiment.
18   The block copolymers of this invention can be represented by
19 the following general formulae:

20                     $(A_1)(A_2)(A_3)\cdots(A_n)$

21 wherein each A is a polymer segment having an average molecular
22 weight from about 100 to about 1,000,000 daltons chosen independently
23 from homopolymers consisting of HDPE, homo and copolymers of cyclic
24 olefins, such as polycyclopentene and polynorbornene, and isotactic,
25 atactic, and syndiotactic poly-1-olefins such as atactic-PP,
26 isotactic-PP, syndiotactic-PP; random copolymers of 1-olefins and
27 diolefins such as ethylene-propylene rubber,
28 ethylene-propylene-hexadiene rubber, ethylene-butene rubber, linear
29 low density polyethylenes, such that no adjacent segments are the
30 same polymer composition.
31   Novel block copolymers of this invention include but are not
32 limited to diblock copolymers such as (HDPE)(EP), (i-PP(EP),
33 (LLDPE)(a-PP), (HDPE)(a-PP), (LLDPE(HDPE) and the like, and triblock

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1 copolymers such as (HDPE)(EP)(HDPE), (HDPE)(a-PP)(HDPE),
2 (HDPE)(EP)LLDPE), (LLDPE)(a-PP)(LLDPE), (HDPE)(a-PP)(LLDPE),
3 (i-PP)(EP)(i-PP), (s-PP)(EP)(s-PP) and the like. It will be recognized
4 to those well versed in the field that the isotactic polypropylene
5 segments contained in the block copolymers of this invention have
6 microstructure defects which are not observed in conventional i-PP
7 materials prepared using titanium Ziegler-Natta catalyst. The
8 microstructure defects which are unique to isotactic polypropylenes
9 prepared using metallocene catalysts arise from 1-3 and 2-1 additions to
10 propylene. The melting points of such materials can vary from $60^{\circ}C$ to
11 $165^{\circ}C$ depending on the total number total defects.
12   The tapered copolymers can be represented by similar general
13 formula where the transitions between idealized polymer segments A_n
14 are gradual. These gradient transitions between segments are
15 represented by arrows.

16   (A_1)--->(A_2)--->(A_3)--->$\cdots\cdots(A_n)$.

17 An example of this would be a polymer prepared by reacting a 50-50
18 mixture of ethylene and propylene with a living catalyst which has a
19 high preference for ethylene over propylene. The tapered polymer
20 obtained in such an experiment would be designated by the following
21 formula:

22   HDPE--->EP--->a-PP

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EXAMPLES

1 Catalyst Preparation. The catalyst used in the following examples
2 was prepared in dry, deoxygenated toluene (5.0 cc) by reacting
3 Cp_2HfMe_2 with one equivalent of [DMAH][B(pfp)$_4$] (where DMAH =
4 PhMe$_2$NH$_+$ and pfp = C_6F_5) at room temperatur for 5-10 minutes. The
5 reaction is known to cleanly produce methane gas and a single
6 ionic catalyst [Cp$_2$HfMe(PhNMe$_2$)][B(pfp)$_4$].

Example 1
First Ethylene then Propylene.

7   The reactor was cooled to 0°C and charged with 400 mls of
8 toluene and 0.30 mmoles of catalyst. Ethylene (4.0 grams; 0.143
9 moles) was added to the reactor. After all the ethylene was
10 consumed, propylene (6 grams; 0.139 moles) was added; after 30
11 minutes the reactor was dropped and the product collected. The
12 crude product contained 50 mole % propylene, had an
13 M_n = 87,000 with a molecular weight distribution of 3.0. The
14 crude product was washed with hexane at room temperature to remove
15 any -PP which was not in the form of block copolymer. The hexane
16 insoluble material contained cyrstalline HDPE (as determined by
17 IR) and 30 mole % propylene; the M_n was 144,000 with a molecular
18 weight distribution of 1.89. The hexane soluble fraction was -
19 PP, did not contain ethylene (by IR), and had an M_n of 63,000 with
20 a molecular weight distribution of 1.47. Based on the extraction
21 studies, it was concluded that 50-60% of the -PP chains were
22 incorporated into a block coplymer under these conditions.

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1 M_n = 87,000 with a molecular weight distribution of 3.0. The crude
2 product was washed with hexane at room temperature to remove any
3 α-PP which was not in the form of block copolymer. The hexane
4 insoluble material contained crystalline HDPE (as determined by IR)
5 and 30 mole % propylene; the M_n was 144,000 with a molecular weight
6 distribution of 1.89. The hexane soluble fraction was α-PP, did
7 not contain ethylene (by IR), and had a M_n of 63,000 with a
8 molecular weight distribution of 1.47. Based on the extraction
9 studies, it was concluded that 50-60% of the α-PP chains were
10 incorporated into a block copolymer under these conditions.

Example 2
First Propylene Then Ethylene

11 The procedure of Example 1 was repeated except propylene was
12 added first. The crude product had 41 mole % propylene (IR), a M_n
13 of 170,000 with a molecular weight distribution of 1.78. A pad was
14 pressed and extracted with hexane for 4 hours. At this point, the
15 material contained 37 mole % propylene and very crystalline HDPE.
16 The pad was further extracted with toluene at room temperature for 50
17 hours with no loss of weight. The extracted "diblock" had a M_n of
18 230,000 and a molecular weight distribution of 1.48 (the hexane
19 solubles were α-PP having a Mn of 125,000 and a molecular weight
20 distribution of 1.72).

Example 3
Molecular Weight Control in Block Copolymer Synthesis

21 Using the procedure in Example 2, 3.0 grams of propylene
22 (0.070 moles) were added to 0.30 mmole of the hafnium catalyst.
23 After the propylene (0.071 moles) was completely consumed, 2.0 grams
24 of ethylene were added to the system. The resulting product was
25 washed with hexane at room temperature to remove any α-PP. The
26 resulting block copolymer had a Mn of 107,000 and a molecular weight
27 distribution of 1.68, and contained 42 mole % propylene by IR
28 spectroscopy.

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Example 4
Effect of Temperature

1   If the temperature is raised the effect is to lower the
2 efficiency of the block formation. The temperature was raised from
3 0°C to 10°C and the blocking efficiency was reduced to less than 10%
4 to 65%. When the temperature was lowered to -5°C, the blocking
5 efficiency improved 78%.

Example 5
The Effect of Increasing the Time
Between the Addition of Monomers

6   A series of block copolymerizations were run at 0°C and the
7 time between the addition of propylene and ethylene was varied from 6
8 to 42 minutes. The crude products were collected, analyzed by GPC
9 and IR, then extracted with hexane at room temperature for 65 hours
10 to remove unblocked α-PP. In a well-behaved system wherein the
11 extraction technique removes all of the α-PP, a logrithmically
12 increase in the percent of hexane extractables with time would be
13 expected. The data of this example is shown in Fig. 1 in graphical
14 form. The Y-axis represents the percent of polypropylene which is
15 incorporated into the block copolymer. The extractables were
16 isolated and analyzed by GPC and IR; they were all pure α-PP. . The
17 correlation is close to the linear result expected so that this
18 technique can be used to evaluate the kinetics of chain loss under a
19 variety of conditions. This result confirms the ability to make true
20 block copolymers, and confirms that hexane extraction is a good
21 measure of block copolymer efficiency for this polymer system.

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Example 6
Preparation of EP

1   In this example, 1.6 grams of propylene (0.037 moles) were
2 added to [Cp$_2$HfMe(L)][B(pfp)$_4$] (0.30 mmole) in 400 cc of
3 toluene at 0°C.   Immediately after the propylene addition, 1.1 grams
4 of ethylene (0.039 moles) was metered in over 3 minutes. After six
5 minutes, the product was recovered yielding 2.7 grams of amorphous EP
6 rubber. The product was non-crystalline by IR; the polymer had a
7 M$_n$ of 96,000 and a molecular weight distribution of 1.69.

Example 7
Preparation of EP

8   In this example, 3.2 grams of propylene (0.074 moles) was
9 added to [Cp$_2$HfMe(L)][B(pfp)$_4$] (0.30 mmole) in 400 cc of
10 toluene at 0°C. Ethylene (2.2 grams; 0.078 moles) was added to the
11 reactor over 5.5 minutes. The product was recovered yielding 5.7
12 grams of EP rubber having a M$_n$ of 155,000, and a molecular weight
13 distribution of 1.48. The IR showed some degree of PE-crystallinity.

Example 8
Preparation of EP-b-HDPE

14   Example 6 was repeated to prepare "living" EP-rubber. After
15 all the monomer had been consumed, ethylene (1.1 grams) was added to
16 prepare the desired block copolymer. The product was recovered
17 yielding 4.25 grams of copolymer. The IR showed PE crystallinity and
18 the polymer had thermoplastic-like properties. The onset of Tg was
19 -52.9°C and the product had a melting point of 119°C. The M$_n$ of
20 the crude product was 161,000 with a molecular weight distribution of
21 1.59.

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1   Example 9.   The intention of this example is to demonstrate
2   that slow chain transfer can be used to catalytically prepare
3   block copolymers.   This is an example of in-situ catalyst
4   recycle leading to the production of mixtures of small
5   amounts of homopolymer and mixtures of multiblock copolymers
6   (AB, ABA, BAB etc).

7   The reactor was cooled to 0°C and charged with 400 mls of
8   toluene and 0.15 mmole of catalyst.   In step 1, propylene
9   (1.5 grams) was added to the well stirred reactor causing a
11 pressure increase of 7 psi.   After 7 minutes the pressure in
12 the reactor dropped to zero and the reactor was vented
13 through a nujol bubbler to remove any residual propylene in
14 the system.   In step 2, ethylene (1.0 grams) was added.   The
15 ethylene was consumed in less than one minute.   After all the
16 ethylene was consumed the reactor was vented.   These
17 sequential steps were repeated 5 more times resulting in
18 similar monomer conversion rates.   The reactor was dropped
19 and the the product was collected yielding 15 grams after
20 drying.   The crude product was analyzed by GPC and had a M_n =
21 122K and a MWD = 2.2.   The melting point was 126°C by DSC and
22 the IR indicated the presence of high crystallinity
23 polyethylene.   A thin pad weighing 1.25 grams was compression
24 molded and extracted with hexane a room temperature for 72
25 hours at room temperature.   The pad was removed, dried and
26 weighed yielding 1.13 grams of insoluble material.   The
27 insoluble material was analyzed by GPC and DSC and had a M_n =
28 171K, a MWD = 1.8 and a melting point of 126°C.   The soluble
29 material was isolated (0.12 grams) and was identified as
30 atactic PP.   The extraction data indicated that 84% of the
31 polypropylene is bonded to insoluble polyethylene segments.
32 The data are not sufficient to detect homo-polyethylene, or
33 to quantify the ratios of the various possible multiblock
34 copolymers.   The observation, however, that the M_n of the
35 crude and extracted products in this experiment are only
36 slightly higher than is typical of a standard A-B sequential
37 addition (M_n = 1201-140K) at the same monomer:catalyst ratio
39 suggests that the chain lifetimes are not sufficiently long
40 to produce high amounts of triblock or other higher order
41 block copolymers.

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1   Example 10.   The reactor was cooled to 0°C and charged with
2   400 mls of toluene and 0.15 mmole of catalyst. In step 1,
3   propylene (1.5 grams) was added to the well stirred reactor
4   causing a pressure increase of 7 psi. After 7 minutes the
5   pressure in the reactor dropped to zero and the reactor was
6   vented through a nujol bubbler to remove any residual
7   propylene in the system. In step 2, ethylene (1.0 grams) was
8   added. The ethylene was consumed in less than one minute.
9   After all the ethylene was consumed the reactor was vented
10   and in step 3 propylene (1.5 grams) was added. The propylene
11   was consumed in 7 minutes and after an addition 20 minute
12   waiting period steps 1,2 and 3 were repeated. The reactor
13   was dropped and 4 grams of crude dry product was isolated.
14   The crude product was analyzed by GPC and had a M_n = 140K and
15   a MWD = 1.7. The IR spectrum indicated the presence of high
16   crystallinity polyethylene. A thin pad weighing 1.07 grams
17   was compression molded and extracted with hexane a room
18   temperature for 72 hours at room temperature. The pad was
19   removed, dried and weighed yielding 0.87 grams of insoluble
20   material. The insoluble material was analyzed by GPC had a
21   M_n = 192K, a MWD = 1.4. The soluble material was isolated
22   (0.20 grams) and was identified as atactic PP by IR and NMR
23   spectroscopy. The extraction data indicated that 81% of the
24   polypropylene is bonded to insoluble polyethylene segments.

25   Example 11.   In this example we describe an attempt to
26   prepare an ABA triblock copolymer where the A-block is high
27   density polyethylene and the B-block is elastomeric atactic
28   polypropylene. We disclose a technique where a small amount
29   of propylene (5% of the amount added in the B-step) is added
30   in a prepolymerization step.   The effect of this is to
31   solubilize the insoluble polyethylene A-segment and prevent
32   precipitation of the living polymer. When this procedure is
33   used a clear, apparently homogeneous reaction mixture is
34   formed. Similar experiments where the prepolymerization step
35   is not used gives a heterogeneous reaction mixture, lower
36   blocking efficiencies and broader molecular weight
37   distributions.

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The reactor was cooled to 0°C and charged with 400 mls of toluene and 0.15 mmole of catalyst. In a prepolymerization step 1, propylene (0.15 grams) was added to the well stirred reactor. After 7 minutes the pressure in the reactor dropped to zero and the reactor was vented through a nujol bubbler to remove any residual propylene in the system. In step 2, ethylene (0.5 grams) was added. After 2 minutes, propylene (3.0 grams) was added to the well stirred reactor causing a pressure increase of 7 psi. The propylene was consumed in 4 minutes at which point the reactor was vented and ethylene (0.5 grams) was added. The reactor was dropped and approximately 4 grams of crude dry product was isolated. The crude product was analyzed by GPC and DSC and had a melting point of 122°C, a Mn = 173K and a MWD = 1.9 (with a bimodal shape). A thin pad weighing 1.295 grams was compression molded and extracted with hexane a room temperature for 72 hours at room temperature. The pad was removed, dried and weighed yielding 1.17 grams of insoluble material. The resulting material has thermoplastic elastomeric properties. The extraction data indicated that 86% of the polypropylene is bonded to insoluble polyethylene segments.

Example12. The reactor was cooled to 0°C and charged with 400 mls of toluene and 0.15 mmole of catalyst. In a prepolymerization step 1, propylene (0.15 grams) was added to the well stirred reactor. After 7 minutes the pressure in the reactor dropped to zero and the reactor was vented through a nujol bubbler to remove any residual propylene in the system. In step 2, ethylene (0.25 grams) was added. After 2 minutes, propylene (3.0 grams) was added to the well stirred reactor causing a pressure increase of 7 psi. The propylene was consumed in 4 minutes at which point the reactor was vented and ethylene (0.25 grams) was added. The reactor was dropped and approximately 3.5 grams of crude dry product was isolated. The crude product was analyzed by GPC and DSC and had a melting point of 122°C, a Mn = 160K and a MWD = 1.8 (with a bimodal shape). A thin pad weighing 1.288 grams was compression molded and extracted with hexane a room temperature for 72 hours at room temperature. The extremely swollen pad was removed, dried and weighed yielding 1.165 grams of insoluble material. The resulting material has thermoplastic elastomeric properties. The extraction data indicated that 88% of the polypropylene is bonded to insoluble polyethylene segments. The insoluble product was analyzed by GPC and had a Mn = 184K and a MWD = 1.6 (with a bimodal shape).

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CLAIMS

1.   A process for the production of block copolymers
comprising:

(i) contacting a first olefinic monomer(s) with a
catalyst which is the reaction product of:

(a) a metallocene component, and

(b) a second component having a cation capable of
donating a proton and a compatible non-coordinating anion to produce a
first living polymer; and

(ii) sequentially adding to said living polymer at least
a second monomer(s) to copolymerize with said first polymer to produce
a multi block copolymer; and

(iii) recovering a block copolymer

2.   The process of claim 1 wherein the block copolymer is a
diblock copolymer.

3.   The process of claim 1 wherein the block copolymer is a
triblock.

4.   The process of claim 1 wherein the catalyst reaction
product is of the formulae:

$$[A-CpMX_1][(C_2B_9H_{11})_2Co]$$
$$[A-CpMX_1(L')][B(C_6F_5)_3(X_3)]$$
$$[(A-CpMX_1)_2X_1][B']$$
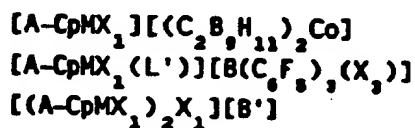
wherein: M is titanium, zirconium or hafnium; (A-Cp) is either
(Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different
substituted or unsubstituted cyclopentadienyl radicals; A' is a
covalent bridging group containing a Group IV-A element; L' is a
neutral Lewis base; X_1 is a hydride radical, hydrocarbyl radical
having from 1 to about 20 carbon atoms, substituted-hydrocarbyl
radical, wherein 1 or more of the hydrogen atoms are replaced with a

halogen atom, having from 1 to about 20 carbon atoms, or organo-metalloid radical comprising a Group IV-A element wherein each of the hydrocarbyl substituents contained in the organo portion of said organo-metalloid, independently, contain from 1 to about 20 carbon atoms; C_1-C_{20} and X_2 is a hydride, halide, hydrocarbyl radical, a C_1-C_{20} hydrocarbyl radical wherein one or more of the hydrogen atoms is replaced by a halogen atom, organometalloid radical wherein each hydrocarbyl substitution in the organo portion contains from 1 to 20 carbon atoms and the metal is a Group IVA metal.

5. The process of claim 4 wherein the catalyst reaction product is represented by the formula:

$$[A-CpMX_1(L')][B(C_6F_5)_3(X_2)]$$

6. The process claim 1, wherein the catalyst is the reaction product bis(cyclopentadienyl) hafnium dimethyl and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

7. The process of claim 1 wherein said steps of reacting, copolymerizing, introducing and repeating are carried out at a temperature of from about -5°C to about 10°C.

8. The process of claim 1 wherein any of said monomers is selected from ethylene, propylene, 1-butene.

9. Olefinic block copolymers having a Mw/Mn of from about 1 to 5 represented by the formula:

$$(A_1)(A_2)(A_3)\cdots\cdots(An)$$

wherein each A represent a polymer segment having an average of Mw of from 100 to about 1,000,000 daltons, each adjacent A represents a different olefinic polymer segment, A being selected from HDPE, atactic-1-olefins, isotactic 1-olefins, syndiotactic 1-olefins, homo-

and copolymers of cyclic olefins, and random copolymers of 1-olefins and diolefins.

10. The olefin block copolymers of claim 9 wherein the polymer segments are selected from are atactic-polypropylene, isotactic-polypropylene and syndiotactic-polypropylene.

11. Olefin block copolymers of claim 11 wherein said block copolymers is a diblock.

12. Olefin block copolymers of claim 11 selected from (HDPE)(EP), (i-PP)(EP), (LLDPE)(a-PP), (LLDPE)(HDPE).

13. Olefin block copolymers of claim 10 wherein said block copolymer is a triblock.

14. Olefin block copolymers of claim 13 selected from (HDPE)(EP)(HDPE), (HDPE)(EP)(LLDPE), (LLDPE)(a-PP)(LLDPE)(HDPE)(a-pp)(LLDPE), (i-PP)(EP)(i-PP)(s-pp)(EP)(s-PP).

15. Mixtures of homopolyolefins, and di- and triblock copolymers, said block copolymers produced by the process of claims 2 and 3.

INTERNATIONAL SEARCH REPORT

International Application No   PCT/US 91/00835

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 08 F 297/08, C 08 F 4/64

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC⁵	C 08 F 4/00, C 08 F 293/00, C 08 F 297/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	DE, A1, 3 826 075 (HOECHST AG) 01 February 1990 (01.02.90), see claims 1-6,9; examples.	1-4,7-11,13,15
A	DE, A1, 3 640 924 (HOECHST AG) 01 June 1988 (01.06.88), see claims 1-4; examples.	1-4,7-11,13
A	US, A, 4 522 982 (EWEN) 11 June 1985 (11.06.85), see claims 1,6,8; examples.	1,4,7-10,15
A	US, A, 4 408 019 (BLUNT) 04 October 1983 (04.10.83), see claim 1; examples (cited in the application).	1,3,4,7-9
A	EP, A1, 0 277 004	1,4-6

* Special categories of cited documents: ¹⁴

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
19 April 1991	2 4. 05. 91

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	M. SOTELO

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document,** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	(EXXON CHEMICAL PATENTS INC.) 03 August 1988 (03.08.88), see claims 1-4,6,7. --	
A	EP, A1, 0 277 003 (EXXON CHEMICAL PATENTS INC.) 03 August 1988 (03.08.88), see claims 1-3,13. ----	1,4

ANHANG	ANNEX	ANNEXE
zum internationalen Recherchen-bericht über die internationale Patentanmeldung Nr.	to the International Search Report to the International Patent Application No.	au rapport de recherche inter-national relatif à la demande de brevet international n°

PCT/US91/00835 SAE 44664

In diesem Anhang sind die Mitglieder der Patentfamilien der im obenge-nannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unter-richtung und erfolgen ohne Gewähr.	This Annex lists the patent family members relating to the patent documents cited in the above-mentioned inter-national search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.	La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche inter-national visée ci-dessus. Les reseigne-ments fournis sont donnés à titre indica-tif et n'engagent pas la responsibilité de l'Office.

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